



# A comparative study of the selective catalytic reduction of NO by propylene over supported Pt and Rh catalysts

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## Abstract

The catalytic performance of Pt and Rh catalysts for the selective catalytic reduction (SCR) of NO by propylene in the presence of excess oxygen has been investigated over catalysts supported on six different metal oxide carriers ( $\text{CeO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ , YSZ,  $\text{ZrO}_2$  and  $\text{W}^{6+}$ -doped  $\text{TiO}_2$ ). It has been found that the nature of the dispersed metal affects strongly the light-off temperature of propylene, the maximum NO conversion to reduction products and the selectivity towards nitrogen. For a given support, Pt catalysts are always more active for both NO reduction and propylene oxidation, but are much less selective towards  $\text{N}_2$ , compared to Rh catalysts. Rhodium catalysts are able to selectively reduce NO even in the absence of oxygen in the feed. However, their activity is suppressed with increasing oxygen feed concentration possibly due to the formation of less reactive rhodium oxides. In contrast, oxygen promotes the *de-NO<sub>x</sub>* activity of platinum catalysts but decreases selectivity towards nitrogen. Results are explained by considering the effects of the nature of the metallic phase and the support on the elementary steps of the propylene-SCR reaction. It is concluded that the catalytic performance of both metals may be improved by proper selection of the support.

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## 1. Introduction

The selective catalytic reduction (SCR) of nitrogen oxides ( $\text{NO}_x$ ) by hydrocarbons (HC) has received worldwide attention as a potentially effective method for the elimination of  $\text{NO}_x$  in the exhaust gases of lean-burn and diesel fueled vehicles [1–4]. The reaction has been studied extensively over zeolite catalysts in the presence of excess oxygen and has given promising results in terms of high activities for NO reduction and relatively wide temperature windows of operation [5–8]. The main disadvantage of zeolite-based catalysts, which limits their potential use in practical applications, is their poor hydrothermal stability. Metal oxide catalysts supported on base oxides, such as alumina [9–12], have also attracted attention due to their high activity and hydrothermal stability, but are active at relatively high temperatures and an inhibition effect is usually observed in the presence of  $\text{SO}_2$  [13,14]. Supported noble metals catalysts, in particular platinum group metals

(PGM), seem to be the most promising candidates for the HC-SCR of  $\text{NO}_x$  because of their high reduction activity at relatively low temperatures [1–4,15], their enhanced resistance against  $\text{SO}_2$ , compared to the metal oxide catalysts [16,17], and their tolerance towards steam [18]. Among the noble metal catalysts investigated, platinum is the most active at low temperatures and, therefore, widely studied. However, Pt-based catalysts are characterized by low selectivity towards  $\text{N}_2$ , which is typically less than 30%. In contrast, Rh-containing catalysts exhibit superior behavior as far as selectivity to  $\text{N}_2$  is concerned but require higher operating temperatures, compared to Pt [3,15,16].

Concerning the mechanism of the HC-SCR reaction of  $\text{NO}_x$  over supported PGM catalysts under lean-burn conditions, several schemes have been proposed, which have been recently reviewed [11,19]. Most researchers agree that the reaction involves dissociative adsorption of NO on the active metal sites followed by recombination of the adsorbed species to yield  $\text{N}_2$  or  $\text{N}_2\text{O}$  [11,19–21]. The chemical state of the noble metal under reaction conditions seems to play a crucial role because active sites for NO dissociation are believed to be reduced surface atoms, such as  $\text{Pt}^0$  or  $\text{Rh}^0$  [2,3,22–24]. The role of the reductant

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is to scavenge adsorbed oxygen atoms and regenerate the catalytically active sites. According to other mechanisms, adsorbed  $\text{NO}_2$  or other intermediates, such as organo-nitro and related species [25–27], play an important role in the  $de\text{-NO}_x$  reaction. Experimental evidence has also been provided for the intermediacy of cyanide ( $-\text{CN}$ ) and/or isocyanate ( $-\text{NCO}$ ) surface species [28–31].

In our previous studies, we have investigated in detail the reduction of NO by CO [23,24,28,32] over Rh catalysts as well as the SCR of NO by propylene over Rh [22,33–35] and Pt [36] catalysts. In the present work, the effects of the nature of the active metallic phase (Pt and Rh) and the support ( $\text{CeO}_2$ ,  $\text{TiO}_2$ ,  $\text{TiO}_2(\text{W}^{6+})$ , YSZ,  $\text{ZrO}_2$  and  $\text{Al}_2\text{O}_3$ ), and also of the oxygen feed concentration on the catalytic performance for the title reaction are investigated. Results are used to extract information related to the mechanism of the reaction over Pt and Rh catalysts, to elucidate the chemical state of the active metal sites and to identify the parameters which determine catalytic activity and selectivity.

## 2. Experimental

Catalysts were prepared employing the wet impregnation method [36] with the use of  $(\text{NH}_3)_2\text{Pt}(\text{NO}_2)_2$  or  $\text{Rh}(\text{NO}_3)_3 \cdot 2\text{H}_2\text{O}$  as metal precursor salts and the following commercial metal oxide powders as supports:  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{CeO}_2$ , YSZ and  $\text{ZrO}_2$ . Titanium dioxide doped with  $\text{W}^{6+}$ -cations, denoted in the following as  $\text{TiO}_2(\text{W}^{6+})$ , has been also used as catalyst support. This material was prepared by the method of solid-state diffusion, using  $\text{TiO}_2$  P-25 (Degussa) and  $(\text{NH}_4)_{12}\text{W}_{12}\text{O}_{41} \cdot 5\text{H}_2\text{O}$  (Alfa) as starting materials. Diffusion of the dopant cation into the crystal matrix of  $\text{TiO}_2$  has been achieved by calcination of the sample at 900 °C, following a procedure which has been reported previously [35]. The nominal metal loading of all catalyst samples thus prepared was 0.5 wt.%. The specific surface area of the supports has been determined employing nitrogen physisorption at the temperature of liquid nitrogen (BET method). Metal dispersion and mean crystallite size were obtained employing  $\text{H}_2$  chemisorption (CO chemisorption for Pt/ $\text{CeO}_2$ ) at room temperature, following a procedure described elsewhere [36]. Results of catalyst characterization are summarized in Table 1. It should be noted that the chemisorption capacity of Pt is significantly suppressed when it is supported on  $\text{TiO}_2$  doped with higher valence cations (e.g.  $\text{W}^{6+}$ ), compared to undoped  $\text{TiO}_2$ , whereas

the opposite is true for Rh ([37] and Refs. therein). This may explain the relatively low values of Pt dispersion estimated for  $\text{Pt}/\text{TiO}_2(\text{W}^{6+})$  and the relatively high values of Rh dispersion estimated for  $\text{Rh}/\text{TiO}_2(\text{W}^{6+})$ , compared to  $\text{Pt}/\text{TiO}_2$  (Table 1).

The catalytic performance of the prepared samples for the SCR of NO by propylene was investigated in the temperature range of 150–550 °C using a feed composition consisting of 0.1% NO, 0.1%  $\text{C}_3\text{H}_6$  and 5%  $\text{O}_2$  (balance He). The effects of inlet oxygen partial pressure on catalytic activity and selectivity have been investigated with the use of variable feed compositions containing 0–10%  $\text{O}_2$ . In all cases, the mass of catalyst loaded to the quartz reactor was 60 mg and the total volumetric flow rate was 200  $\text{cm}^3/\text{min}$  ( $W/F = 0.018 \text{ g s cm}^{-3}$ ). On-line analysis of reactants and products was accomplished with the use of a gas chromatograph (Shimadzu GC-9A) and a  $\text{NO}/\text{NO}_x$  analyzer (Teledyne 911/912). Chromatographic separation of  $\text{N}_2$ ,  $\text{O}_2$  and  $\text{CO}$  has been achieved using a molecular sieve 5A column while  $\text{N}_2\text{O}$ ,  $\text{C}_3\text{H}_6$  and  $\text{CO}_2$  were analyzed using a Porapak-Q column. The concentrations of NO and  $\text{NO}_2$  at the effluent of the reactor were continuously monitored with the use of the  $\text{NO}_x$  analyzer. High purity reaction gases were obtained from Meissner-Griesheim. Details on the apparatus and procedures employed can be found elsewhere [35,36].

## 3. Results

### 3.1. De- $\text{NO}_x$ performance of Pt and Rh catalysts under lean-burn conditions

Typical results of catalytic performance tests obtained over  $\text{Al}_2\text{O}_3$ -supported Pt and Rh catalysts are presented in Fig. 1A and B, respectively, where the conversions of NO ( $X_{\text{NO}}$ ) and  $\text{C}_3\text{H}_6$  ( $X_{\text{C}_3\text{H}_6}$ ) as well as the yields of  $\text{N}_2$ ,  $\text{N}_2\text{O}$  and  $\text{NO}_2$  are plotted as functions of reaction temperature. It is observed that conversion of propylene over  $\text{Pt}/\text{Al}_2\text{O}_3$  catalyst (Fig. 1A) increases sharply with increasing reaction temperature above ca. 200 °C and reaches completion at ca. 265 °C. This is accompanied by a parallel increase of the yields of  $\text{N}_2$  and  $\text{N}_2\text{O}$  which pass through maxima at ca. 270 °C, i.e., at temperatures somewhat higher than the light-off temperature of propylene, defined here at the temperature at which  $X_{\text{C}_3\text{H}_6}$  exceeds 90%. Under these conditions, conversion of NO to reduction products ( $\text{N}_2$  and  $\text{N}_2\text{O}$ ) reaches a maximum value of 34% and then progressively decreases upon further increase of temperature.

Table 1  
Characteristics of the supported Pt and Rh catalysts investigated

Support material	Pt catalysts (0.5 wt.%)			Rh catalysts (0.5 wt.%)	
	Metal oxide	Specific surface area ( $\text{m}^2/\text{g}$ )	Pt dispersion (%)	Mean Pt crystallite size ( $\text{\AA}$ )	Rh dispersion (%)
$\text{CeO}_2$	3	46	22	43	25
$\text{Al}_2\text{O}_3$	83	60	17	80	13
$\text{TiO}_2$	50	85	12	88	12
YSZ	12	64	16	100	10
$\text{TiO}_2(\text{W}^{6+})$	15	30	34	100	10
$\text{ZrO}_2$	4	65	15	35	31

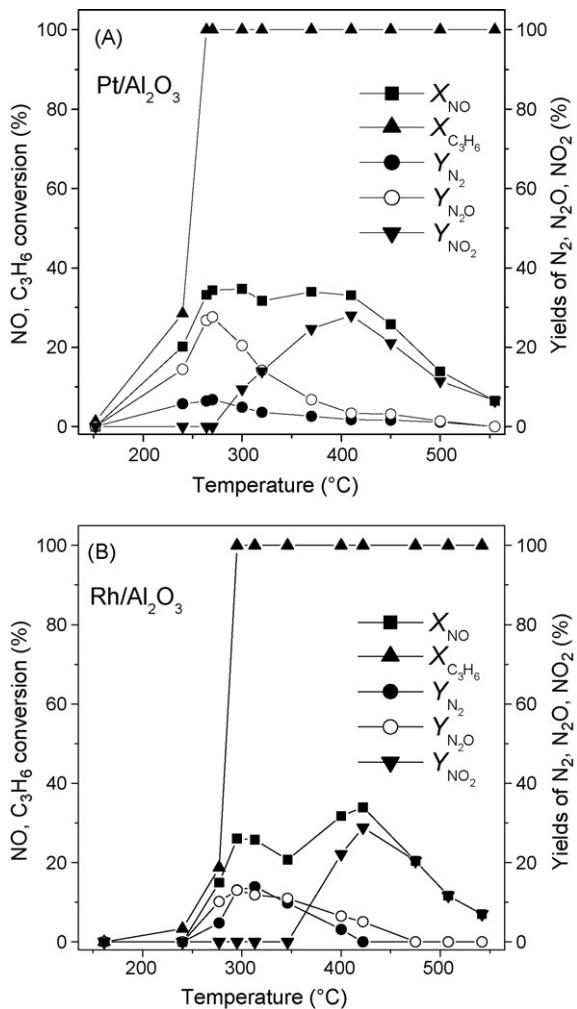


Fig. 1. Conversions (%) of NO ( $X_{NO}$ ) and propylene ( $X_{C_3H_6}$ ) and yields (%) of  $N_2$  ( $Y_{N_2}$ ),  $N_2O$  ( $Y_{N_2O}$ ) and  $NO_2$  ( $Y_{NO_2}$ ) obtained over (A)  $Pt/Al_2O_3$  and (B)  $Rh/Al_2O_3$  catalysts as functions of reaction temperature. Feed composition: 0.1% NO, 0.1%  $C_3H_6$  and 5% O<sub>2</sub> (balance: He).

This is accompanied by an increase of the yield of  $NO_2$ , which goes through a maximum at 410 °C and decreases again, following thermodynamic equilibrium constraints (Fig. 1A).

Comparison of results obtained over  $Pt/Al_2O_3$  (Fig. 1A) with the corresponding ones obtained over  $Rh/Al_2O_3$  (Fig. 1B) shows the following differences: (a) oxidation of propylene is initiated at higher temperatures over the Rh catalyst and reaches completion at ca. 295 °C, i.e., about 30 °C higher than that over Pt; (b) maximum conversion of NO to reduction products is lower for Rh (26%), compared to Pt (34%) catalyst; (c) temperature at maximum NO conversion to reduction products ( $T_{max}$ ) is higher for Rh (295 °C), compared to Pt (270 °C); (d) selectivity towards  $N_2$  ( $S_{N_2}$ ) at  $T_{max}$  is significantly higher over Rh (50%) compared to Pt (20%); (e) formation of  $NO_2$  is initiated at substantially lower temperatures over the Pt catalyst.

The effect of reaction temperature on the  $de\text{-}NO_x$  performance of Pt and Rh catalysts dispersed on the other metal oxide supports investigated (not shown for brevity) is qualitatively similar to that shown in Fig. 1A and B,

respectively. In all cases, reduction of NO is closely related to the activation of propylene. At temperatures lower than light-off temperature, conversion of NO is practically zero. It is only when conversion of the hydrocarbon starts to increase that conversion of NO to reduction products is initiated.  $X_{C_3H_6}$  and  $X_{NO}$  then tend to rise in parallel until NO reduction reaches a maximum rate at a temperature somewhat higher than that required for complete conversion of propylene. This maximum in NO conversion, which is always observed under HC-SCR conditions over noble metal catalysts, reflects changes in the relative rates of the propylene/NO and propylene/O<sub>2</sub> reactions as the temperature is varied [19,20].

The effects of the nature of the metal oxide carrier on the  $de\text{-}NO_x$  performance of dispersed Pt and Rh are summarized in Fig. 2, where catalysts are compared to each other with respect to  $X_{NO}$ ,  $S_{N_2}$  and  $T_{max}$ . It is observed that, for Pt catalysts, maximum NO conversion to reduction products varies in the range of 18–40%, with  $X_{NO}$  decreasing in the

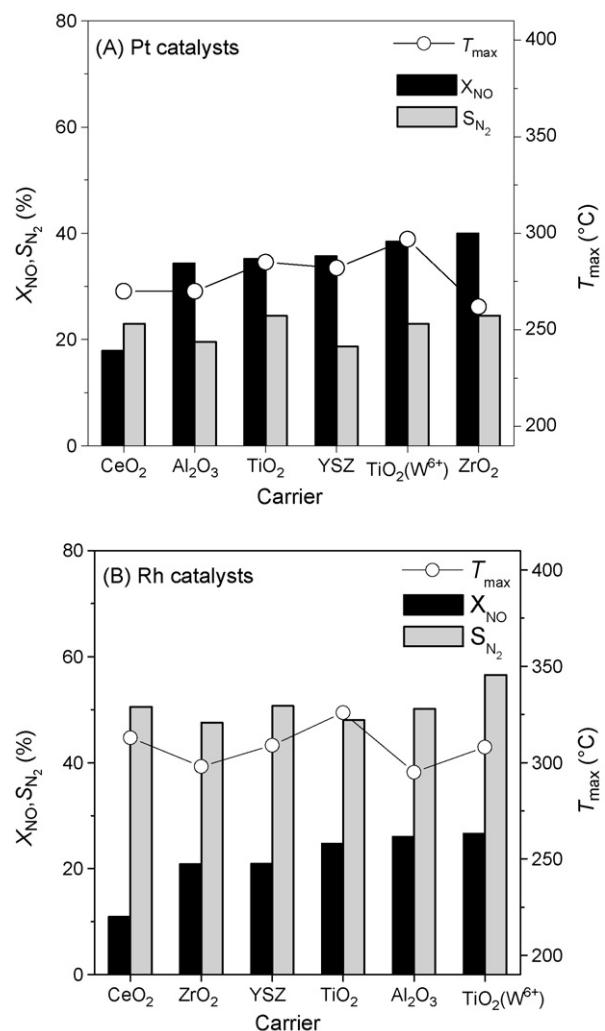


Fig. 2. Effects of the nature of the support on the maximum NO conversion to reduction products ( $X_{NO}$  to  $N_2 + N_2O$ ), selectivity towards nitrogen ( $S_{N_2}$ ) and temperature of maximum NO conversion ( $T_{max}$ ) obtained from (A) Rh and (B) Pt catalysts dispersed on the indicated carriers. Experimental conditions as in Fig. 1.

order of  $\text{Pt}/\text{ZrO}_2 \sim \text{Pt}/\text{TiO}_2(\text{W}^{6+}) > \text{Pt}/\text{YSZ} \sim \text{Pt}/\text{TiO}_2 \sim \text{Pt}/\text{Al}_2\text{O}_3 > \text{Pt}/\text{CeO}_2$  (Fig. 2A). In the case of Rh catalysts (Fig. 2B),  $X_{\text{NO}}$  is generally lower than that over Pt samples, varying in the range of 11–27%. Ranking of catalytic activity, with respect to the nature of the support, is different, compared to that observed for Pt, the main differences being the relatively low activity of  $\text{ZrO}_2$ - and the relatively high activity of  $\text{Al}_2\text{O}_3$ -supported catalysts. In contrast to what is observed for  $X_{\text{NO}}$ , selectivity towards  $\text{N}_2$  does not depend strongly on the nature of the support but mainly on the nature of the dispersed metal, varying between 19 and 25% for Pt catalysts (Fig. 2A) and between 48 and 56% for Rh catalysts (Fig. 2B). Regarding  $T_{\text{max}}$ , it is systematically lower for Pt ( $260\text{--}295^\circ\text{C}$ ) compared to Rh ( $295\text{--}325^\circ\text{C}$ ) catalysts (Fig. 2).

### 3.2. Effects of oxygen partial pressure

The effects of oxygen partial pressure on the activity and selectivity of Pt- and Rh-containing catalysts have been investigated in detail. Oxygen feed concentration was varied in the range of 0–10%, whereas the concentrations of NO and  $\text{C}_3\text{H}_6$  were kept constant at 1000 ppm. Reaction temperature was set at  $280^\circ\text{C}$ , selected based on the results of Fig. 2. At this temperature, conversion of propylene is high or complete, production of  $\text{NO}_2$  is negligible and formation of reduction products is measurable for all Pt and Rh catalysts investigated.

#### 3.2.1. Platinum catalysts

The influence of inlet oxygen partial pressure ( $P_{\text{O}_2}$ ) on the  $de\text{-NO}_x$  performance of  $\text{Pt}/\text{Al}_2\text{O}_3$  is illustrated in Fig. 3A. It is observed that in the absence of oxygen in the feed the catalyst is practically inactive. The same is true for feed compositions containing small concentrations of oxygen (lower than ca. 0.3%). Conversion of propylene becomes measurable for  $P_{\text{O}_2} > 0.3\%$  and thereafter increases abruptly with increasing oxygen feed concentration.  $X_{\text{C}_3\text{H}_6}$  reaches 100% for  $P_{\text{O}_2} = 5\%$  and is maintained at this level for higher oxygen inlet pressures. Activation of propylene is accompanied by the onset of NO reduction towards  $\text{N}_2$  and  $\text{N}_2\text{O}$ . Conversion of NO increases progressively with increasing  $P_{\text{O}_2}$  above ca. 0.3% and reaches maximum value of ca. 20% for  $P_{\text{O}_2} = 5\%$ . Selectivity towards nitrogen is relatively high (50–60%) for low oxygen concentrations ( $P_{\text{O}_2} < 0.5\%$ ) but progressively decreases to ca. 15% with increasing  $P_{\text{O}_2}$  to 10% (Fig. 3A).

Results of similar experiments conducted over Pt catalysts dispersed on all metal oxide supports investigated are summarized in Fig. 4. It is observed that the inlet oxygen partial pressure, at which light-off of propylene is observed, depends appreciably on the nature of the support employed. In particular, conversion of propylene is measurable over  $\text{Pt}/\text{CeO}_2$  even in the absence of oxygen in the feed, whereas oxygen concentrations higher than ca. 2% are required for propylene activation over  $\text{Pt}/\text{TiO}_2$  and  $\text{Pt}/\text{TiO}_2(\text{W}^{6+})$  catalysts (Fig. 4A). In all cases, conversion of propylene reaches 100% for  $P_{\text{O}_2} > 5\%$ . Regarding conversion of NO to reduction products, it becomes measurable for oxygen concentrations similar to those required for activation of propylene and progressively

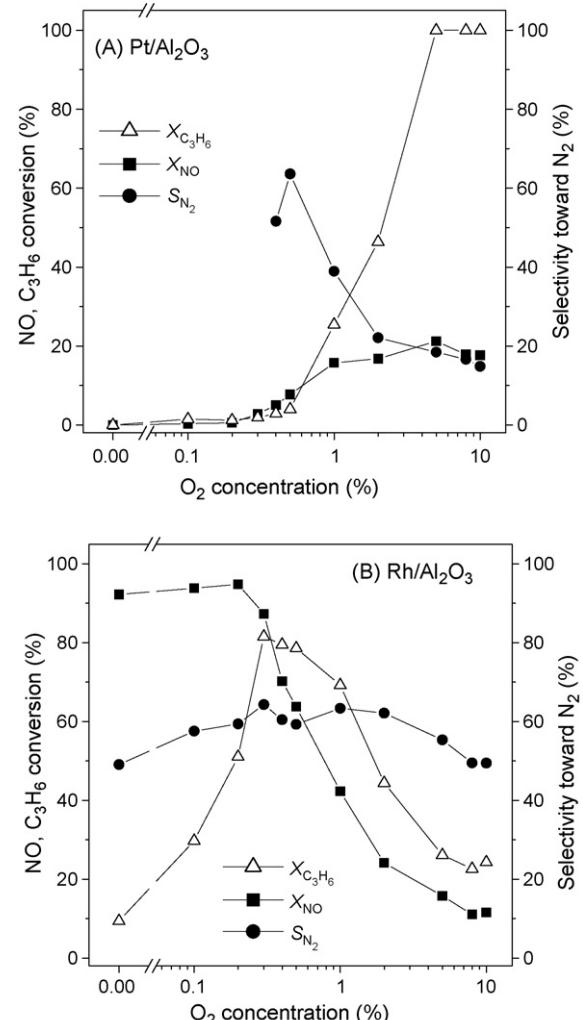


Fig. 3. Effect of oxygen inlet partial pressure on the catalytic performance of (A)  $\text{Pt}/\text{Al}_2\text{O}_3$  and (B)  $\text{Rh}/\text{Al}_2\text{O}_3$  catalysts. Feed composition: 0.1% NO, 0.1%  $\text{C}_3\text{H}_6$  and (0–10)%  $\text{O}_2$ ;  $T = 280^\circ\text{C}$ .

increases with increasing  $P_{\text{O}_2}$  (Fig. 4B). This behavior reflects the promotional effect of oxygen on the  $de\text{-NO}_x$  activity of Pt catalysts. Depending on the nature of the support, conversion of NO goes through a maximum at certain oxygen pressure and then slightly decreases upon further increasing  $P_{\text{O}_2}$ .

Selectivity towards nitrogen for a given  $P_{\text{O}_2}$  does not depend appreciably on the nature of the metal oxide carrier (Fig. 4C). An exception is  $\text{Pt}/\text{TiO}_2$ , the selectivity of which is typically higher (by ca. 10% units), compared to the rest of the examined catalysts. In contrast, selectivity depends strongly on oxygen concentration and decreases almost linearly with increasing  $\log(P_{\text{O}_2})$  for all Pt catalysts investigated. In particular,  $S_{\text{N}_2}$  takes values around 60% for  $P_{\text{O}_2} < 0.5\%$  and drops to less than 20% with increasing  $P_{\text{O}_2}$  to 10% (Fig. 4C).

#### 3.2.2. Rhodium catalysts

The effect of inlet oxygen concentration on the  $de\text{-NO}_x$  performance of  $\text{Rh}/\text{Al}_2\text{O}_3$  at  $280^\circ\text{C}$  is shown in Fig. 3B. In contrast to what is observed for Pt (Fig. 3A), the Rh catalyst is very active for the reduction of NO by propylene in the absence

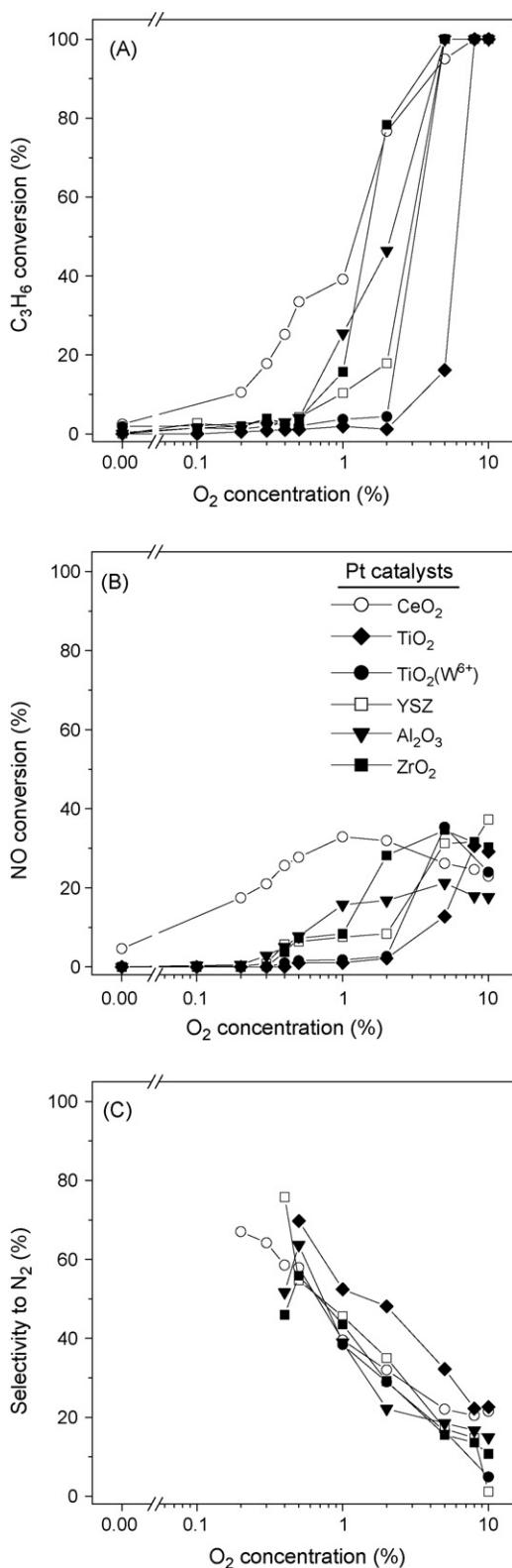


Fig. 4. Effects of oxygen inlet partial pressure on the conversion of propylene (A), conversion of NO to reduction products (B), and selectivity towards N<sub>2</sub> (C) over Pt catalysts dispersed on the indicated supports. Experimental conditions as in Fig. 3.

of oxygen in the feed. In particular, conversion of NO to reduction products (N<sub>2</sub> + N<sub>2</sub>O) is about 90% at P<sub>O<sub>2</sub></sub> = 0%, where propylene conversion is around 8%. Increasing oxygen

concentration from 0 to 0.3% does not affect significantly X<sub>NO</sub>, which slightly increases from 90 to 95%, but results in a progressive increase of X<sub>C<sub>3</sub>H<sub>6</sub></sub> from 8 to ca. 80%. This indicates that, under these conditions, reduction of NO by propylene occurs in parallel with hydrocarbon oxidation by oxygen. Further increase of P<sub>O<sub>2</sub></sub> from 0.3 to 10% results in progressive decrease of X<sub>C<sub>3</sub>H<sub>6</sub></sub> from 80 to 22% (Fig. 3B). This is accompanied by a drastic decrease of NO conversion, which drops to ca. 11% for P<sub>O<sub>2</sub></sub> > 8%. In contrast to what is observed for Pt (Fig. 3A), selectivity towards N<sub>2</sub> is not significantly affected by oxygen concentration in the feed. In particular, S<sub>N<sub>2</sub></sub> increases from ca. 50% in the absence of oxygen to about 60% for P<sub>O<sub>2</sub></sub> in the range of 0.2–2.0%, i.e., when X<sub>C<sub>3</sub>H<sub>6</sub></sub> is high, and then decreases again to ca. 50% for higher O<sub>2</sub> concentrations (Fig. 3B).

Similar catalytic performance tests were carried out for all supported Rh catalysts investigated and results are summarized in Fig. 5. It is observed that all samples are able to activate propylene (Fig. 5A) and reduce NO (Fig. 5B) in the absence of oxygen in the feed, with X<sub>NO</sub> ranging from 70% over Rh/TiO<sub>2</sub> to 98% over Rh/YSZ, at P<sub>O<sub>2</sub></sub> = 0% (Fig. 5B). Addition of 0.1–0.3% O<sub>2</sub> in the feed results in a significant increase of the conversion of propylene, which is accompanied by a further increase of X<sub>NO</sub> to 93–100%. For most Rh catalysts investigated, conversion of propylene is complete for P<sub>O<sub>2</sub></sub> = 0.3–0.5% and decreases at higher P<sub>O<sub>2</sub></sub>. This is accompanied by a parallel decrease of X<sub>NO</sub>, which drops to less than 12% at P<sub>O<sub>2</sub></sub> = 10%, for all Rh catalysts investigated. Results of Fig. 5B show that the de-NO<sub>x</sub> performance of supported Rh catalysts under oxygen-rich conditions can be significantly affected by the nature of the support employed. For example, conversion of NO and propylene over Rh/CeO<sub>2</sub> at P<sub>O<sub>2</sub></sub> = 2% is 16 and 47%, respectively, while it is much higher for Rh/TiO<sub>2</sub>(W<sup>6+</sup>) (X<sub>NO</sub> = 47% and X<sub>C<sub>3</sub>H<sub>6</sub></sub> = 83%) under the same experimental conditions (Fig. 5).

Selectivity of Rh catalysts towards nitrogen ranges between 40 and 65% exhibiting a weak, broad maximum at P<sub>O<sub>2</sub></sub> = 0.2–2.0% (Fig. 5C). In contrast to what is observed for Pt catalysts, S<sub>N<sub>2</sub></sub> depend appreciably on the nature of the support and less strongly on oxygen feed concentration. It is of interest to note that catalyst ranking with respect to nitrogen selectivity is inverted at P<sub>O<sub>2</sub></sub> ~ 0.3%, i.e., at inlet oxygen partial pressures where maximum conversion of propylene is achieved (Fig. 5A). In particular, although for P<sub>O<sub>2</sub></sub> ≤ 0.3% the Rh/CeO<sub>2</sub> and Rh/TiO<sub>2</sub>(W<sup>6+</sup>) catalysts are the most and least selective samples of this series, respectively, the opposite is true for P<sub>O<sub>2</sub></sub> ≥ 0.3% (Fig. 5C). As a result, under oxygen-rich conditions, Rh/CeO<sub>2</sub> exhibits the lowest NO conversion and selectivity, while Rh/TiO<sub>2</sub>(W<sup>6+</sup>) is the most active and selective Rh catalyst investigated (Fig. 5).

### 3.3. Effect of pretreatment conditions on catalytic performance

Results presented in Figs. 3–5 show that the oxygen feed concentration affects, to a significant extent, the de-NO<sub>x</sub> performance of supported Pt and Rh catalysts. As will be

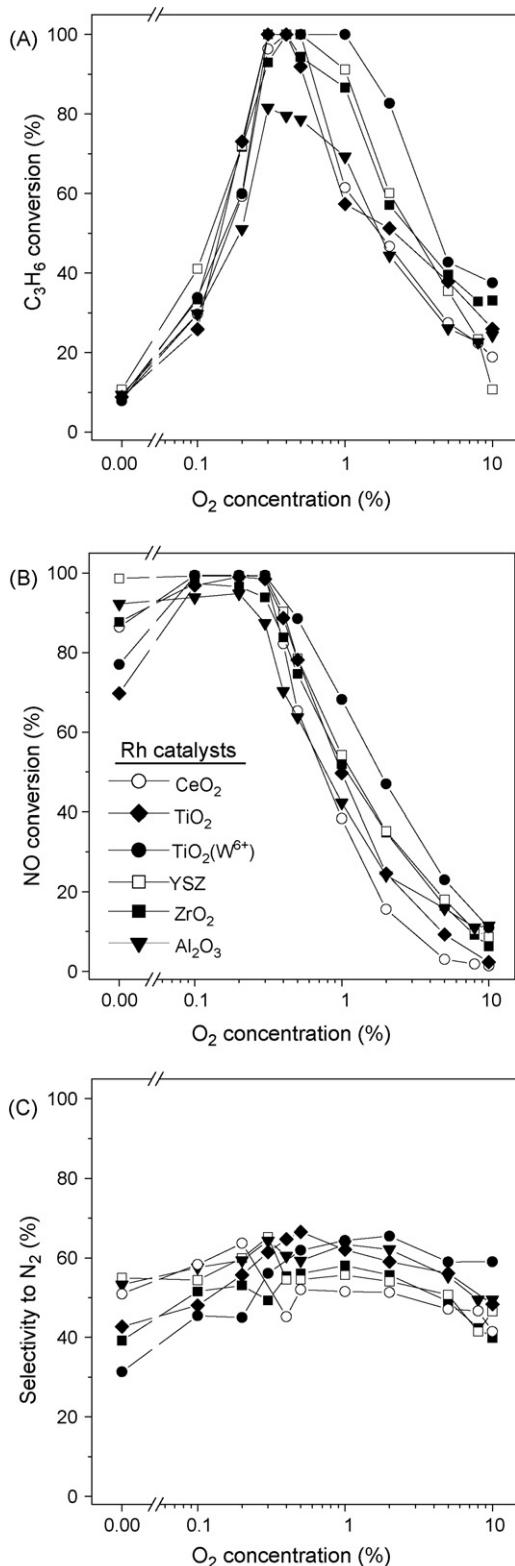


Fig. 5. Effects of oxygen inlet partial pressure on the conversion of propylene (A), conversion of NO to reduction products (B), and selectivity towards N<sub>2</sub> (C) over Rh catalysts dispersed on the indicated supports. Experimental conditions as in Fig. 3.

discussed below, this may be attributed to the influence of feed composition on the oxidation state of the dispersed noble metals under reaction conditions. In order to investigate this

issue, catalytic performance tests were conducted with the use of catalysts either pre-reduced in 5%H<sub>2</sub>/He flow at 550 °C for 1 h or pre-oxidized under 20%O<sub>2</sub>/He flow at 550 °C for 2 h. Experiments were performed over TiO<sub>2</sub>(W<sup>6+</sup>)-supported Pt and Rh catalysts, which were among the most active and selective samples investigated (Figs. 2, 4 and 5). Catalytic performance was evaluated with the use of a feed composition consisting of 0.1% NO, 0.1% C<sub>3</sub>H<sub>6</sub> and 5% O<sub>2</sub> for a period of 50 h. The reaction temperature was kept constant at 290 °C for the Pt catalyst and at 315 °C for the Rh catalyst, and was chosen so as to be close to T<sub>max</sub>, where maximum SCR activity is observed for each catalyst (Fig. 2).

Results obtained over Pt/TiO<sub>2</sub>(W<sup>6+</sup>) are illustrated in Fig. 6A, where the conversions of NO and propylene obtained from the pre-reduced (pre-red.) and the pre-oxidized (pre-ox.) catalyst are plotted as functions of time-on-stream. It is

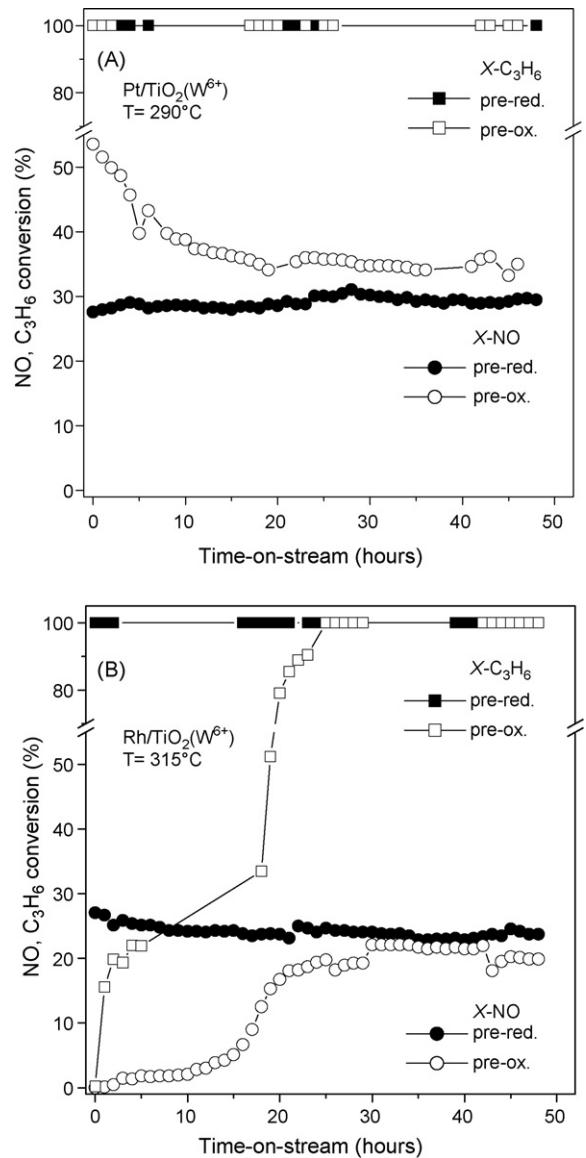


Fig. 6. Conversions of NO and C<sub>3</sub>H<sub>6</sub> obtained from pre-oxidized (open symbols) and pre-reduced (filled symbols) catalysts as functions of time-on-stream. (A) Pt/TiO<sub>2</sub>(W<sup>6+</sup>) catalyst at 290 °C and (B) Rh/TiO<sub>2</sub>(W<sup>6+</sup>) catalysts at 315 °C. Feed composition: 0.1% NO, 0.1% C<sub>3</sub>H<sub>6</sub> and 5% O<sub>2</sub>.

observed that the pre-reduced sample exhibits a very stable propylene-SCR activity during a period of 50 h-on-stream. In particular, conversion of NO to reduction products is about 30% and conversion of propylene is complete for the whole reaction period investigated. Selectivity towards nitrogen (not shown for clarity) is also very stable, taking values of  $S_{N_2} = 31 \pm 2\%$  throughout the test. It should be noted that formation of  $NO_2$  was negligible under the present experimental conditions.

Results obtained from the pre-oxidized  $Pt/TiO_2(W^{6+})$  catalyst are also shown in Fig. 6A. It is observed that the initial conversion of NO (54%) is much higher, compared to that observed for the pre-reduced sample. However, this difference is mainly due to the formation of  $NO_2$ , which seems to be favored over the pre-oxidized catalyst. Prolonged exposure to the reaction mixture results in a progressive decrease of NO conversion, as a result of a suppression of  $NO_2$  formation, and drops to ca. 35% after about 20 h-on-stream.  $X_{NO}$  does not further change for prolonged exposure to the reaction mixture while  $S_{N_2}$  remains stable at  $34 \pm 2\%$ . Conversion of propylene was 100% throughout the experiment. Comparison of the NO conversion curves obtained from the pre-reduced and the pre-oxidized sample shows that, under the present reaction conditions,  $X_{NO}$  shifts asymptotically to the same level, irrespective of the pretreatment procedure employed.

Similar long-term catalytic performance tests have been conducted over the  $Rh/TiO_2(W^{6+})$  catalyst at  $315^\circ C$  and results obtained are shown in Fig. 6B. It is observed that, as in the case of Pt, the pre-reduced Rh catalyst exhibits a relatively constant  $de-NO_x$  activity, with  $X_{NO}$  being stable at ca. 24% for about 50 h-on-stream. Conversion of propylene is complete and selectivity towards NO remains constant at  $60 \pm 1.5\%$  throughout the experiment. Pre-oxidation of the catalyst leads to a completely different behavior. Conversion of propylene is initially very small and increases progressively to ca. 30% after about 15 h-on-stream. During this period, conversion of NO is also very low, with  $X_{NO}$  increasing gradually from zero to about 5% after 15 h. Further exposure to the reaction mixture causes a relatively rapid increase of  $X_{C_3H_6}$ , which reaches 100% after ca. 25 h-on-stream. In the same time period, conversion of NO increases substantially and is stabilized at ca. 20%. The catalyst light-off also results in a small decrease of selectivity towards  $N_2$ , which drops from ca. 58 to 54%. As in the case of the Pt catalyst, results of Fig. 6B show that the steady-state activity and selectivity of Rh does not depend, practically, on the pretreatment conditions employed.

#### 4. Discussion

Results of the present study are in general agreement with those reported in the literature for the propylene-SCR of NO in excess oxygen over Pt and Rh catalysts: Rh exhibits relatively lower activity but higher selectivity towards nitrogen, compared to Pt, and requires higher reaction temperatures for hydrocarbon activation and for the achievement of maximum NO conversion (Figs. 1 and 2) [1,38]. Of special interest are the differences observed between Pt and Rh

catalysts with respect to the effects of oxygen feed composition, nature of the support and pretreatment conditions on activity and selectivity (Figs. 3–6). These results can be discussed by considering the mechanism of HC-SCR over supported noble metal catalysts. It is widely accepted [11,19,39] that the role of the metal is to adsorb dissociatively NO on adjacent, reduced metal sites:



The so-formed nitrogen atoms may then combine to form  $N_2$  or react with an undissociated NO molecule to yield  $N_2O$  in the gas phase:



It should be noted that NO adsorbed on a unique free site (Eq. (1)) will not dissociate if this free site is enclosed by occupied sites, e.g.  $N_{(a)}$  or  $O_{(a)}$  [11]. Interaction between neighbouring  $NO_{(a)}$  and  $O_{(a)}$  species results in the formation of  $NO_2$ :



Regarding gas-phase oxygen, it competes with NO for the same adsorption sites:



Accumulation of adsorbed oxygen produced via Eqs. (2) and (6) results in poisoning of the catalytically active sites and, therefore, an oxygen atom scavenger is necessary for the NO reduction to proceed. In HC-SCR this is accomplished by the hydrocarbon (propylene in the present case), which effectively reduces oxidized metal sites via formation of a series of hydrocarbonaceous intermediates, thereby regenerating the catalytically active sites [19,22,35,40]:



The importance of this step is reflected in the fact that, under oxygen-rich conditions, NO reduction always coincides with hydrocarbon combustion (e.g. Fig. 1).

#### 4.1. De- $NO_x$ activity of Rh and Pt catalysts

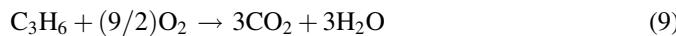
According to the reaction mechanism described above, an effective  $de-NO_x$  catalyst should be characterized by high activity for NO dissociation (Eqs. (1) and (2)), which is the key step for NO reduction, and also by high activity for hydrocarbon oxidation in a manner, which allows removal of adsorbed oxygen and preservation of the metallic state of the catalyst (Eq. (7)). Regarding dissociative adsorption of NO, it is well known that it is favored over Rh catalysts, compared to other noble metals, such as Pt or Pd. This has been attributed to the correct placement of the metal's fermi level relative to the molecular orbitals of adsorbed NO [41]: the fermi level of Rh is

located above the antibonding orbitals of NO, while in Pt (or Pd) it is below. Thus, additional charge is transferred from the Rh surface into the antibonding orbitals of NO, thereby weakening the N–O bond, which is not the case for Pt. This property of Rh is reflected on its unique ability to form negatively charged adsorbed NO species, which are supposed to be the active ones for NO dissociation [23,24,42].

Results presented in Figs. 3 and 4 clearly indicate the superior performance of Rh, compared to Pt, for catalyzing reduction of NO in the absence of oxygen in the feed. For example, conversion of NO over the Rh/Al<sub>2</sub>O<sub>3</sub> catalyst is ca. 90% at  $P_{O_2} = 0\%$ , where propylene conversion is around 8% (Fig. 3B). This stoichiometry indicates that the following overall reactions take place over Rh, in the absence of oxygen:



Interestingly, addition of small oxygen concentrations in the feed ( $P_{O_2} \leq 0.3\%$ ) does not affect significantly  $X_{NO}$ , which slightly increases from 90 to 95%, but results in a progressive increase of  $X_{C_3H_6}$  from 8 to ca. 80% (Fig. 3B). This implies that, under these conditions, reduction of NO by propylene (Eq. (8)) runs in parallel with hydrocarbon oxidation by oxygen:

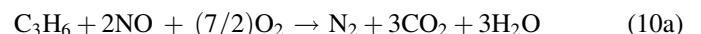


The same is true for all Rh catalysts investigated (Fig. 5). It may then be suggested that, for relatively low  $P_{O_2}$  values, competition of oxygen (Eq. (6)) and NO (Eqs. (1) and (2)) for the same adsorption sites is in favor of the latter molecule. This could be attributed to the relatively high concentration of  $N_{(a)}$  species present on Rh surface under these conditions, which inhibits  $O_2$  adsorption. As a result, propylene is selectively consumed for the removal of oxygen atoms formed by NO dissociation (Eq. (2)), thereby promoting reduction of NO (Eq. (8)) versus propylene oxidation (Eq. (9)). A similar behavior has been reported for the reduction of NO by CO in the presence of oxygen over polycrystalline noble metal foils [41], where it was shown that NO is best able to compete with  $O_2$  for CO over Rh, compared to Pt or Pd [41].

The drawback in the *de-NO<sub>x</sub>* performance of Rh catalysts is that their activity decreases significantly for higher oxygen feed concentrations (Fig. 5). The volcano-type dependence of  $X_{C_3H_6}$  on  $P_{O_2}$  (Fig. 5A) can be explained by taking into account the effect of oxygen concentration on the oxidation state of rhodium and the concomitant effects on its catalytic performance. It is well known that exposure of reduced Rh catalysts to an oxidizing environment results in the formation of Rh oxide phases, which are much less reactive than metallic Rh [43–45]. For example, the rate of oxidation of light hydrocarbons has been found to increase with increasing  $P_{O_2}$  and then, at a critical  $P_{O_2}$  value, where surface oxidation of Rh is initiated, it decreases abruptly and becomes negative-order in oxygen [46,47]. Results of Fig. 5A also indicate the existence of two regimes corresponding to a reduced and an oxidized surface, respectively: for  $P_{O_2}$  lower than ca. 0.3%, the Rh surface is reduced and the catalyst is active for propylene

oxidation and, consequently, for NO reduction. For higher oxygen concentrations, there seems to be a transition from a reduced Rh surface to an oxidized one, which results in the observed suppression of propylene oxidation (Fig. 5A) and NO reduction activity (Fig. 5B). This reasoning is supported by the results of Fig. 6B, which clearly show that, initially, the pre-oxidized Rh/TiO<sub>2</sub>(W<sup>6+</sup>) catalyst is practically inactive for the title reaction. This is probably due to the presence of Rh<sub>2</sub>O<sub>3</sub> formed during the pre-oxidation step, which exhibits low activity for hydrocarbon oxidation [46,47]. The long induction period, which is necessary for the catalyst to restore its steady-state activity, reflects the slow reduction of rhodium oxide under the experimental conditions employed (Fig. 6B).

Regarding the activity of platinum catalysts, results presented in Fig. 4 show that they are not able to catalyze reduction of NO in the absence of oxygen (Eq. (8)), due to their inability to activate propylene (Fig. 4A) under the present experimental conditions. However, in the presence of oxygen in the feed, Pt promotes HC-SCR of NO according to the following overall stoichiometric reactions:



This behavior can be explained by considering that the extent of the HC-SCR reaction over Pt catalysts depends on the ratio of hydrocarbon to oxygen surface coverages ( $\theta_{HC}/\theta_O$ ) [48]: in the absence of oxygen in the feed, i.e., when  $\theta_{HC}$  is very high, hydrocarbonaceous species are deposited on the catalyst surface thereby suppressing NO reduction. However, as the oxygen inlet concentration increases, the hydrocarbonaceous species are removed from the surface by reacting with adsorbed oxygen (Eq. (7)) and the active sites become available for NO reduction (Eqs. (1) and (2)). This is evidenced by the increase of  $X_{C_3H_6}$  with increasing  $P_{O_2}$ , which is accompanied by an increase of  $X_{NO}$  (Fig. 4). Depending on the experimental conditions employed (e.g. reaction temperature, nature of the reductant, etc.), a volcano-type dependence of NO and HC conversions is often observed for Pt catalysts [48–50]. This is because at high oxygen concentrations poisoning of the surface by hydrocarbonaceous species (at zero or low  $P_{O_2}$ ) is replaced by poisoning by  $O_{(a)}$  species (at high  $P_{O_2}$ ), both leading to blocking of the surface for NO adsorption and reaction.

In contrast to what is observed for Rh catalysts, platinum does not lose its activity under strongly oxidizing conditions. This is clearly shown in Fig. 6A, which shows that pre-oxidation of Pt/TiO<sub>2</sub>(W<sup>6+</sup>) does not suppress either propylene oxidation or NO conversion. In contrast, the pre-oxidized catalyst is much more active, initially, for NO oxidation indicating that oxidized Pt species catalyze effectively reaction (5).

#### 4.2. Selectivity towards nitrogen

One of the most striking differences between the investigated Pt and Rh catalysts is related to the dependence of N<sub>2</sub>-selectivity on oxygen partial pressure. In particular,  $S_{N_2}$

decreases drastically with increasing  $P_{O_2}$  over Pt (Fig. 4C), while it remains practically unaffected for Rh catalysts (Fig. 5C). According to the reaction mechanism discussed above,  $N_2$  and  $N_2O$  are formed via common pathways (Eqs. (1)–(4)) and, therefore, the observed dependences of  $S_{N_2}$  on  $P_{O_2}$  should be explained by taking into account the effects of oxygen feed concentration on the relative population and recombination rates of  $NO_{(a)}$ ,  $N_{(a)}$  and  $O_{(a)}$  species. For Pt catalysts, results of Fig. 4C indicate that selectivity is mainly influenced by the relative rates of reactions (3) and (4): for low inlet oxygen pressures, where both adsorption and dissociation of NO are easier, the population of adsorbed nitrogen atoms is high and the possibility for their recombination towards  $N_2$  (Eq. (3)) is increased. At higher oxygen concentrations, where  $\theta_O$  is higher, the population of undissociated NO is increased due to the limited number of neighbouring free reduced sites. As a result, the possibility of reaction of  $N_{(a)}$  with  $NO_{(a)}$  (Eq. (4)) is enhanced and  $S_{N_2}$  decreases.

The above reasoning does not apply for Rh catalysts where  $N_2$ -selectivity does not depend, practically on oxygen feed concentration (Fig. 5C) although  $X_{NO}$  varies substantially with  $P_{O_2}$  (Fig. 5B). This implies that the primary influence of oxygen concentration is related to the cleavage of the N–O bond (Eq. (2)) rather than on surface reactions between  $NO_{(a)}$  and  $N_{(a)}$  (Eqs. (3) and (4)). In particular, increasing  $\theta_O$  results in a decrease of the number of sites available for NO dissociation, without affecting subsequent formation of  $N_2$  and  $N_2O$ . In contrast to Pt, it seems that Rh promotes the fast dissociation of molecularly adsorbed NO and, therefore,  $\theta_{NO}$  does not vary significantly with increasing  $P_{O_2}$ , as in the case of Pt. This reasoning is supported by experimental [41] and theoretical [51] studies, which have shown that Pt is less able to dissociate NO, compared to Rh.

#### 4.3. Support effects

Comparison of the results obtained over the Pt and Rh catalysts in the presence of excess oxygen (Figs. 1 and 2) shows that the nature of the support affects substantially the light-off temperature of propylene, the maximum NO conversion to reduction products and, to a lesser extent, selectivity towards nitrogen. The observed differences in catalytic performance cannot be explained by considering the relatively small differences in the noble metal crystallite size (Table 1) and, therefore, should be attributed to effects of the support on the chemisorptive and catalytic properties of the dispersed metal [36]. It is of interest to note that both Pt and Rh catalyst are less active when supported on  $CeO_2$ , compared to the other supports investigated (Fig. 2). In addition, Pt/ $CeO_2$  exhibits an exceptional behavior, compared to the other Pt catalysts studied, being the only one which shows measurable activity for both  $C_3H_6$  oxidation and NO reduction at low oxygen partial pressures (Fig. 4). This may be attributed to the high reducibility of ceria and the availability of active surface oxygen which, as discussed in our previous study [36], may efficiently activate propylene even in the absence of gas-phase oxygen. The ability of  $CeO_2$  to activate propylene at low  $P_{O_2}$

values (Fig. 4A) results in high NO conversions, making Pt/ $CeO_2$  the most active Pt catalyst for the SCR of NO in the  $P_{O_2}$  range of 0–2% (Fig. 4). However, for higher oxygen inlet pressures,  $X_{NO}$  decreases significantly and for  $P_{O_2} > 8\%$ , the ceria-supported sample exhibits a relatively low  $de-NO_x$  performance (Fig. 4B). This implies that, under these conditions, Pt/ $CeO_2$  promotes the unselective, complete oxidation of propylene (Eq. (9)) rather than SCR of NO (Eq. (8)). The same is true for Rh/ $CeO_2$  catalyst (Figs. 2 and 5), indicating that the use of a highly reducible metal oxide support decreases the  $de-NO_x$  performance of supported noble metal catalysts.

On the other hand, the  $TiO_2(W^{6+})$ -supported Pt and Rh catalysts are among the most active samples investigated (Fig. 2). This is in agreement with our previous results, where it was shown that the Rh/ $TiO_2(W^{6+})$  catalyst is very active for the SCR of NO by propylene [34,35] and also for the reduction of NO by CO [28,32]. The improved catalytic performance of this catalyst, compared to that of, for example, undoped Rh/ $TiO_2$ , has been attributed to the higher ability of the  $W^{6+}$ -doped support to adsorb and progressively oxidize propylene, thereby producing efficient oxygen atom scavenger species, which regenerate the catalytically active  $Rh^0$  sites [34,35]. An additional beneficial effect of  $W^{6+}$ -doping of  $TiO_2$  has been related to the electronic type modification of supported rhodium crystallites, which affects the adsorptive properties towards NO and leads to higher rates of NO dissociation [28,32], the latter being the main reaction step for the formation of  $N_2$  over supported noble metal catalysts.

It is of interest to note the relatively strong support effect on catalytic performance for experiments conducted under variable oxygen inlet partial pressures (Figs. 3–5). For Rh catalysts, the oxygen feed concentration at which  $X_{C_3H_6}$  and  $X_{NO}$  start to decrease due to the formation of the less active surface oxides varies from one support to another. For example, although  $X_{C_3H_6}$  goes through a maximum at  $P_{O_2} = 0.3\%$  for Rh/ $Al_2O_3$ , oxygen concentrations higher than 1.0% can be used before the Rh/ $TiO_2(W^{6+})$  catalyst loses its activity (Fig. 5A). This indicates that the resistance of dispersed Rh crystallites towards oxidation depends appreciably on the nature of the metal oxide support employed. This observation is in general agreement with results reported previously for the oxidation of light hydrocarbons over Rh catalysts supported on a variety of different metal oxide carriers [47]. It was found that rhodium supported on  $TiO_2(W^{6+})$  or YSZ exhibited the highest combustion activities and the highest resistance to oxidation, compared to other supports investigated. This behavior could not be explained by structure sensitivity considerations and has been attributed to interactions between the metal crystallites and the oxide carrier [47]. The catalysts with higher activity (due to the support) were found to require higher oxygen partial pressures in order to form the catalytically less active surface Rh oxide.

For Pt catalysts, the nature of the support affects significantly the oxygen partial pressure at which propylene activation is initiated (Fig. 4A). For example, although Pt/ $CeO_2$  shows measurable propylene conversion even in the absence of

oxygen in the feed, oxygen concentrations higher than 2.0% are necessary in the cases of Pt/TiO<sub>2</sub> and Pt/TiO<sub>2</sub>(W<sup>6+</sup>) catalysts. Propylene combustion starts when the activation energy barrier to break the Pt–O bond is overcome and its extent depends on the  $\theta_{\text{HC}}/\theta_{\text{O}}$  ratio, as discussed above. In our previous study [21], it has been found that the nature of the support affects the chemisorptive properties of Pt towards NO and propylene, as well as the population, thermal stability and reactivity of the adsorbed species. The enhanced catalytic performance of Pt/ZrO<sub>2</sub>, compared to Pt/Al<sub>2</sub>O<sub>3</sub> and Pt/CeO<sub>2</sub> (Fig. 2A), has been attributed to several factors including the ability of the former catalyst to activate NO at lower temperatures, to maintain platinum in its reduced state and to decompose nitrates at lower temperatures. Regarding interaction with propylene, it was proposed that Pt/ZrO<sub>2</sub> is capable of activating adsorption and partial oxidation of C<sub>3</sub>H<sub>6</sub> on its surface by providing oxygen species from ZrO<sub>2</sub>. This process was proposed to take place in a controlled manner, which does not lead to unselective, complete oxidation of propylene, as seems to be the case for Pt/CeO<sub>2</sub>.

## 5. Conclusions

The SCR of NO by propylene has been investigated over Pt and Rh catalysts supported on CeO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, YSZ, ZrO<sub>2</sub> or TiO<sub>2</sub>(W<sup>6+</sup>). It has been found that the nature of the dispersed metal affects strongly the light-off temperature of propylene, the maximum NO conversion to reduction products and the selectivity towards nitrogen. For a given support, Pt catalysts are always more active in the presence of excess oxygen for both NO reduction and propylene oxidation, but are much less selective towards N<sub>2</sub>, compared to Rh catalysts. The nature of the support affects substantially the NO reduction activity of both Pt and Rh catalysts and, to a lesser extent, N<sub>2</sub>-selectivity.

Rhodium catalysts are inherently more active and selective than platinum catalysts and, for relatively low oxygen inlet partial pressures, they are able to fully convert NO to reduction products with N<sub>2</sub>-selectivities typically higher than 50%. This is attributed to the unique ability of reduced Rh to promote dissociative adsorption of NO which under these conditions, is not significantly affected by the presence of gas-phase oxygen. Under more severe oxidizing environments, Rh catalysts lose their activity but maintain selectivity at the same high levels. This has been explained by considering the fact that for high oxygen feed concentrations the number of available active sites is decreased due to the formation of less reactive surface oxides. As a result, the de-NO<sub>x</sub> performance of Rh catalysts is mainly determined by the resistance of dispersed metal crystallites towards oxidation, which can be improved with the use of certain supports such as TiO<sub>2</sub>(W<sup>6+</sup>).

Platinum catalysts are not able to catalyze propylene-SCR of NO in the absence of oxygen or in the presence of relatively low inlet oxygen partial pressures, possibly due to the accumulation of hydrocarbonaceous intermediates on the metal's surface, which hinder adsorption and dissociation of NO. However, the reaction is promoted by higher oxygen feed concentrations, where activation of propylene enables efficient regeneration of

the catalytically active sites. The observed decrease of N<sub>2</sub>-selectivity with increasing oxygen feed concentration indicates that it depends on the relative rates of the N<sub>(a)</sub> + N<sub>(a)</sub> → N<sub>2(g)</sub> and N<sub>(a)</sub> + NO<sub>(a)</sub> → N<sub>2O(g)</sub> surface reactions, the latter being favored under higher coverages of adsorbed atomic oxygen. The nature of the support affects significantly the de-NO<sub>x</sub> performance of dispersed Pt crystallites, mainly by controlling the extent of the unselective oxidation of propylene by oxygen.

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